Preloading Hydrous Ferric Oxide into Granular Activated Carbon for Arsenic Removal

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Introduction

Throughout the world, arsenic is creating potentially serious environmental problems for humans and other living organisms. Most reported arsenic problems are found in groundwater supply systems and are caused by natural processes such as mineral weathering and dissolution of metal oxide deposits that can contain traces of arsenic, and this has resulted from a change in the geochemical environment to a reductive condition (*1*, *2*). Arsenic contamination is also caused byhumanactivities such as mining wastes, petroleum refining, sewage sludge, agricultural chemicals, ceramic manufacturing industries, and coal fly ash (*3*–*5*). In early 2001, the U.S. Environmental Protection Agency published a revised arsenic standard of 10 μg/L in drinking water. All public water systems must have complied with this 10 μg/L standard by 2006, although waivers allow some small water systems to achieve compliance at a later date. Thus, there is great need to devise new and innovative technologies that are inexpensive to use, easy to operate, and durable through long-term use.

Compared to other conventional techniques such as oxidation, coagulation/ precipitation, filtration, ion exchange, membrane/reverse osmosis, and biological treatment, adsorption has the following advantages (*1*): it usually does not need a large volume or additional chemicals for treatment (*2*); it is easier to set up as a POE/POU (point of entry/point of use) arsenic removal process.

Studies have revealed that iron (III) has a high affinity toward inorganic arsenic species, and it is very selective to arsenic in the sorption process (*6*, *7*). Recent research has focused on removing arsenic with iron (hydr)oxides as adsorbents or iron-bearing adsorbents. Hydrous ferric oxide (HFO) is one of the promising iron (hydr)oxides for removing both arsenate and arsenite from aqueous phase due to its high iso-electric points (8.1), high specific surface area, and selectivity for arsenic species (*8*). HFO has exhibited surface

areas of about 350–600 m_2/g which is much greater than those of other crystallized iron oxides such as goethite or magnetite (<150 m_2/g) (*9*), and HFO with such high surface area is generally perceived as amorphous. Dixit and Hering (*8*) also reported that HFO can remove arsenite with the same efficiency as arsenate at the crossover pH of 7.5–8.5, while at pHs below cross-over point, HFO removes more As(V), and above this pH, HFO removes more As(III). In contrast, more crystalline iron oxides remove more As(V) than As(III) across the full pH range. However, the hydrous ferric oxide made by Dixit and Hering (*8*) was a suspension that was not suitable for use in column applications due to its nongranular colloidal nature, which incurred low hydraulic conductivity (*10*).Toovercome this disadvantage, granulation techniques have been pursued. Granular ferric hydroxide (GFH) consist of a poorly crystallized _-FeOOH(250–300m_2/g surface area; 75–80% porosity) (*11*, *12*). It was synthesized from ferric chloride solution by neutralization and precipitation with sodium hydroxide, followed by centrifugation and granulation under high-pressure. There are no drying procedures in the preparation, so GFH pores are filled with water, and this offers a high amount of adsorption sites and thus high adsorption capacity. But suppliers havecommented that these iron oxide granules can crumble and disintegrate when they experience prolonged use, and the operations of these GFH or GFO media often involve weekly or monthly backwash. For example, Selvin et al. (*13*) reported that GFH with a media particle size at 0.8–2.0 mm needed a backwashing every 5000 bed volumes. Without backwashing, a significant amount of head loss pressure builds up in the system (*13*).

In order to overcome the crumbling nature of GFH, ironbearing adsorbents such as iron oxide-coated sands (*14*), activated carbon (*15*, *16*), cellulose sponge (*17*), or cation exchange beads (*18*) have been investigated for arsenic removal. In a DeMarco et al. (*18*) study, porous cation exchange resins could obtain an iron loading of 25% based on dry bead weight, and 50% of the iron loading was in the form of FeOOH. Gu et al. (*19*) employed a GAC based iron containing adsorbents. This media was made in two steps, first Fe(II) was adsorbed onto GAC, then the Fe(II) was oxidized to Fe(III) byO_2, H_2O_2, or NaClO. When lignite based carbon was employed, the iron loading could reach 7.9%. They proposed that the impregnated iron was mostly in coordination with various functional groups on GAC, but

not in polymeric iron hydroxide form. The adsorbent could remove arsenic to 7500 bed volumes before reaching 10 μg/L As breakthrough when the influent water contained 50 μg/L of As. The results herein have extended the bed life of ironloaded GAC beyond that by selectively incorporating HFO as discussed below. This research aimed to take advantage of both the high selectivity ofHFOfor arsenic and the skeletal strength of granular activated carbon (GAC). The high surface area of GAC could offer more reactive sites for iron loading. Andthe stable structure ofGACcould preclude the crumbling phenomenon and commensurate backwashing that mere iron oxides may face. Another reason for using a GAC-based system is that a number of the water utilities that must deal with arsenic-contaminated water may already have installed GAC beds to remove trace organic compounds.

In this research, HFO was incorporated into the GAC through incipient wetness via an impregnation protocol. First, the pores of the porous support were saturated with aqueous metal salt solution; then the impregnated support were dried and calcined in order to convert the metal salt to metal (hydro)oxide. It had been reported, for example, that 10–12% Cu impregnation could be achieved via this method (*20*, *21*).

The research herein also built on the collaborative work of our team, in which we have been devising iron-tailored GAC media via a variety of preparation and complexing protocols (*15*). What distinguishes this research from the collaborative work is that this work focused on implanting specifically HFO via incipient wetness impregnation within the GAC, and then characterizing the HFO. Compared to evaporation or precipitation protocol in the collaborative research (*15*), the incipient wetness impregnation applied two steps: one for iron adsorption onto GAC, and another for the formation of iron hydr(oxides). Specifically, iron solution and GAC were equilibrated for 24 h before a controlled curing step was carried out to convert the adsorbed iron into desired iron hydr(oxides) products while with evaporation or precipitation protocol, iron adsorption, and conversion occurred simultaneously.

The objectives of this study were to (1) incorporate homogeneously active HFO into the pores of GAC through an incipient wetness impregnation technique and confirm that the loading was indeed HFO; (2) test the hypothesis that preloadedHFOachieved greater arsenic adsorption capacity than did preloaded iron that was not HFO; (3) understand

the adsorption behavior of the media through physicochemical characterization techniques.

Experimental Section

Water Source. Synthetic arsenic-containing water was prepared for rapid small-scale column tests with deionized water. This water contained 0.3 mM $NaHCO_3$, 0.01 M NaCl and 300-2000 μg/L As(V). Unless otherwise stated, the pH of the synthetic water was maintained at 6.5 (0.2 by adding droplets of 0.1 M of NaOH or HCl.

Natural groundwater originated from the well of the Cool Sandy Beach Community Water System of Rutland, MA (named Rutland water hereafter). The total arsenic in this groundwater was 60 μg/L with about 45 μg/L of As(V) and 15 μg/L of As(III). Characteristics of the groundwater have been presented in Table 1.

Media Preparation. Iron nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$] was employed as a precursor for iron oxide incorporation into the pores of granular-size porous GAC. The GAC used was SuperDarco (SD), a thermally tailored lignite carbon developed at Penn State (*22*, *23*) with grain sizes of U.S. mesh no. 100 × 140 (148–105 μm; median 126 μm).

The following tailoring procedure was developed to achieve homogeneous impregnation: (1) 1.0–1.5mLof ferric nitrate solution at concentrations of 0.5–1g/mLwas dispersed over 1 g of dried GAC and mixed thoroughly, (2) GAC was then dried at room temperature for 24 h before placement in a rotary evaporator for curing (Fe oxide/hydroxide precipitation) at temperatures of 60, 80, or 90 °C for 12 h. (3) after Fe oxide/hydroxide precipitation, the GAC was cooled toroomtemperature then washed thoroughly with deionized water. The washed GACs were dried at room temperature for 24 h prior to use. By this protocol, the Fe oxide/hydroxide precipitation inside the pore structure of the GAC occurred at elevated temperature in the acidic condition without adding NaOH. Parenthetically, the loading, curing, and washing protocols precluded subsequent nitrate leaching as verified by monitoring the effluent nitrate levels during minicolumn tests.

Carbon sample nomenclature has been identified by their %iron contents and initial curing temperature. For example, Fe (*11*)-SD-@80 was GAC SuperDarco iron-loaded at 80 °C

with an iron content of 11% by mass

Characterization of Materials. X-ray diffraction (XRD) patterns were obtained using Philips X'Pert MPD system, which was equipped with Cu KR radiation (40 kV, 30 mA) with a 0.02° step size and 2.5 s step time over the range 10° < 2θ < 70°

Pore volume distribution of GACs were determined by adsorption of argon vapor onto GAC samples by means of isotherms with progressively increasing relative pressures from 10^{-6} to 0.993atm/atmbyASAP2010 units (Micromeritics Instrument Corporation, Norcross, GA).

Arsenic Sorption As a Function of pH. Tocompare arsenic sorption capacities as a function ofpHfor two different media prepared at different temperature, As (V) and As (III) adsorption experiments were conducted. These tests consistently employed 0.1 g/L media, and an arsenic concentration of 3mg/Lin several 125mLpolyethylene bottles. Sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$) or sodium arsenite ($NaAsO_2$) standards of 1000 mg/L as arsenic were used to prepare the arsenate or arsenite stock solutions. The pH was adjusted to prescribed value between 3-11 for each sample using small volumes of acid (HNO_3, 0.1 M) or base (NaOH, 0.1 M) stock solutions. All samples were mixed in a rotary shaker at 150 rpm and 20 (0.5 °C. After 8 h of shaking, the pH of the samples was readjusted to the target pH conditions. All samples were then shaken again in the rotary shaker for 24 h, and then the remaining aqueous phase arsenic was monitored.

Mini-Column Tests. Mini-column test employed a 1 mL syringe (diameter: 6 mm, length: 10 cm) with an empty bed contact time (EBCTs) of 1 min. In accordance with the proportional diffusivity similitude (*24*), the mini-column tests with 1 min EBCT (100 × 140 mesh) simulated a full-scale EBCT of 8.4 min for U.S. mesh no. 12 × 40 (1700–425 μm; median 1060 μm), or 3.5 min for U.S. mesh no. 20 × 50 (850–300 μm; median 440 μm) at full scale.

Chemical Analysis. When arsenic concentrations were less than 300 μg/L, total As was determined with a Shimadzu atomic absorption spectrophotometer (AA-6601F) unit with